PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

A16

Applicant's or agent's file reference 3628+3798PTWO/AG/la	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/EP 03/06592	International filing date *(day/month/year)* 23.06.2003	Priority date *(day/month/year)* 21.10.2002
International Patent Classification (IPC) or both national classification and IPC H01M4/90		
Applicant IDEA LAB S.R.L. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 4 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 5 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the opinion
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
21.05.2004	07.01.2005
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Del Piero, G Telephone No. +49 89 2399-8579

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP 03/06592

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, Pages

1-16 as originally filed

Claims, Numbers

1-32 received on 06.12.2004 with letter of 29.11.2004

Drawings, Sheets

1/7-7/7 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).

   ☐ the language of publication of the international application (under Rule 48.3(b)).

   ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   ☐ contained in the international application in written form.

   ☐ filed together with the international application in computer readable form.

   ☐ furnished subsequently to this Authority in written form.

   ☐ furnished subsequently to this Authority in computer readable form.

   ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:

   ☐ the claims, Nos.:

   ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-32
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-32
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-32
	No:	Claims	

2. Citations and explanations

   see separate sheet

V.

The subject-matter of the current claims is neither disclosed in nor fairly derivable from the state of the art on record.

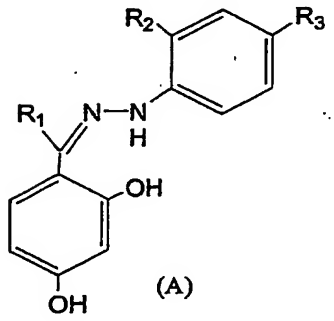
Present claim 1 is directed to subject-matter novel over the accidental disclosure of the S. Lenka et al. paper, which contemplates polymers (including the polymer now excluded by the disclaimer introduced in the amended claim 1) useful as selective ion exchange-resins.

The provision of Pt-free catalysts for electrochemical cells which are efficient in terms of open voltage and power justifies the acknowledgment of an inventive step.

CLAIMS

1. Nitrogen-oxygen-carbon polymers obtained by condensation of a 4-{1-[(2,4-di(substituted)-phenyl)-hydrazono]-alkyl}-benzene-1,3-diol with a 3,5-disubstituted phenol and formaldehyde or paraformaldehyde in the presence of either a basic (e. g. NaOH) or acid (e. g. HCl) catalyst in water/alcohol mixtures as solvent and at a temperature comprised between 20-150 °C and having an average (number) molecular weight comprised between 1000 and 50000.

2. Polymers according to claim 1 wherein the 4-{1-[(2,4-di(substituted)-phenyl)-hydrazono]-alkyl}-benzene-1,3-diol is a compound of formula (A):

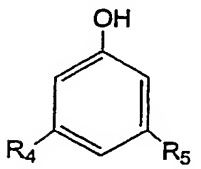


(A)

wherein R_1 is chosen in the group consisting of: hydrogen and a hydrocarbon radical, having from 1 to 10 carbon atoms, possibly halogenated;

R_2 and R_3 each independently represent an electron-withdrawing group selected in the group consisting of hydrogen, halogen, acyl, ester, carboxylic acid, formyl, nitrile, sulphonic acid, linear or branched alkyl or aryl groups, having from 1 to 15 carbon atoms, optionally functionalised with halogens or joined to each other to form one or more condensed cycles with the phenyl ring, and nitro groups.

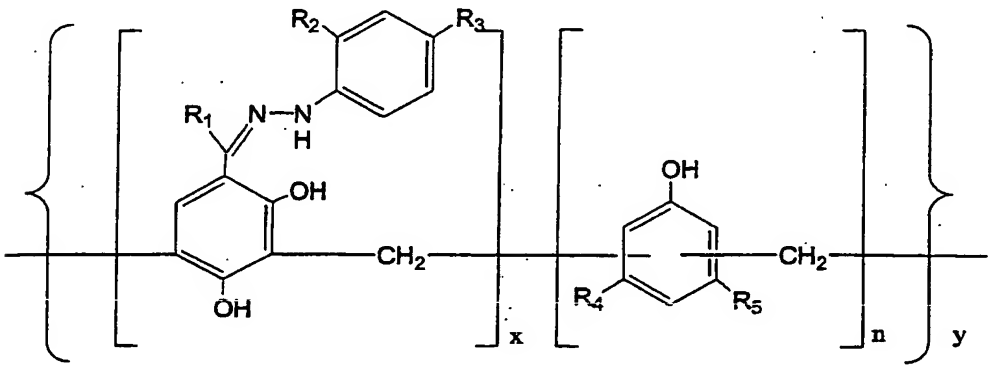
3. Polymer according to claims 1 and 2 wherein the 3,5-disubstituted phenol is a compound of formula (B):



(B)

wherein R_4 and R_5 each independently represent an electron-donating group selected in the group consisting of hydrogen, hydroxyl, ether, amines, aryl and linear and branched alkyl groups, having from 1 to 15 carbon atoms.

4. Polymers according to Claims 1 – 3 having general formula (C)



(C)

wherein y can vary from 2 to 120, x can vary between 1 and 2, n can vary between 1 and 3 and R_1, R_2, R_3, R_4 and R_5 are as above defined.

5. Metal complexes consisting of a polymer according to Claims 1 – 4 and a metal salt.

6. Metal complexes according to Claim 5 wherein the metal salt is chosen in the group consisting of iron-, cobalt- and nickel-carboxylates, -halides, -alcoholates, -acetylacetonates, -formates, -oxalates, -malonates, and analogous organic salts and mixtures thereof or -carbonates, -oxides and -bicarbonates, and mixtures thereof.

7. Complexes according to Claim 6 chosen in the group consisting of: Fe-, Co- and Ni-acetates (and mixture thereof).

8. Catalysts consisting of the complexes according to claims 5 – 7 wherein the metal is reduced either in the solid state with H_2 or in fluid solution systems with appropriate reducing agents.

9. Catalysts consisting of the complexes according to claims 5 – 7 wherein the said metal complexes are pyrolysed at a temperature between 500 and 1000 °C, preferentially 800 °C, under inert gas protection (for example N_2, Ar) for about 2 hours.

10. Electrodes (anodes and cathodes) consisting of the catalysts according to

Claims 8 – 9 and a suitable conductive support.

11. Anodes consisting of the catalysts according to Claims 8 – 9 and comprising binary or ternary combinations of Fe, Co and Ni and a suitable conductive support.

12. Cathodes consisting of the catalysts according to Claims 8 – 9 and comprising Ni or Co and a suitable conductive support.

13. A process for preparing a nitrogen-oxygen-carbon polymer according to Claims 1 – 4 wherein said reaction is carried out by condensation of a 4-{1-[(2,4-di(substituted)-phenyl)-hydrazono]-alkyl}-benzene-1,3-diol with a 3,5-disubstituted phenol and formaldehyde or paraformaldehyde in the presence of a basic catalysts.

14. A process according to claim 13 wherein said reaction is carried out in the presence of an acid catalyst.

15. A process according to claims 13 and 14 wherein said reaction is carried out in the temperature range from about 20 to about 150 °C and in the pH range from about 1 to about 14.

16. A process according to claims 13 – 15 wherein said reaction is carried out in either a one-pot or cascade procedure using as separated components a 4-acyl/formyl-benzene-1,3-diol, a 2,4-disubstituted phenylhydrazine, a 3,5-disubstituted phenol and formaldehyde or paraformaldehyde.

17. A process for preparing a complex according to claims 5 – 7 by dissolving a polymer according to Claim 1 – 3 and one or more salts in an appropriate solvent or mixture of solvents, preferentially acetone, in the temperature range from about 20 °C to about 60 °C and submitting the obtained product to reduction..

18. A process according to Claim 17 wherein a mixture of metal salts chosen in the group consisting of nickel(II), iron(II) and cobalt(II) salts, alone or in binary or ternary combinations in a preferred stoichiometric ratio is used.

19. A process according to Claim 18 wherein the metal(s) loadings are in the range of about 0.5 % to about 10 % of the total elements plus metal weight.

20. A process according to Claims 17 - 19 wherein the reduction step is performed with a flow of H_2 at a temperature between 350 °C and 400 °C for 1-2 hours.

21. A process according to Claims 17 – 19 wherein the reduction step is performed on the complex dispersed in a solvent, with an aqueous solution of hydrazine, or a solution of a tetrahydroborate salt $[Y]BH_4$, wherein Y is Li^+, Na^+, K^+, NR_4^+, PPN^+ and R_4 is as defined in Claim 3 and PPN^+ is bis(triphenylphosphoranylidene)ammonium, at a temperature between 0 °C and 20 °C for 30 minutes-1 hour.

22. A process for preparing a catalyst according to Claims 8 – 9 wherein the metal-doped polymers P-M are pyrolysed at temperatures ranging from 500 to 1000 °C under inert gas protection (for example N_2, Ar) for 1-2 hours.

23. A process for preparing an electrode according to Claims 10 - 11 in the form of anode for fuel cells, involving mixing together the metal doped polymer materials and either a porous carbon support material or other conductive support materials prior to the reduction treatment according to Claims 20 – 21.

24. A process according to claim 23 wherein a single metal or a binary or ternary combinations of nickel, iron and cobalt in a preferred stoichiometric ratio, with metal loadings in the range of about 0.5 % to about 10 % of the total elements plus metal weight are used.

25. A process for preparing an electrode according to Claims 10 and 12 in the form of alcohol-tolerant cathodes for fuel cells, comprising mixing together the metal doped polymer and either a porous carbon support material or other conductive support materials prior to heat-treatment at temperatures ranging from about 500 °C to about 1000 °C under inert gas protection (for example N_2, Ar) for 1-2 hours.

26. A process according to Claim 25 wherein the metal doped polymer contains a metal or a mixture of metals with metal loadings in the range of about 0.5 % to about 10 % of the total carbon plus metal weight.

27. Anodes for Direct Oxidation Fuel cells (DOFC) or Direct Alcohol Fuel Cells (DAFC), formed with a catalysed carbon substrate according to Claims 23 - 24 containing metals chosen in the group consisting of iron, cobalt and nickel.

28. Alcohol-tolerant cathodes for Direct Oxidation Fuel cells (DOFC), or Direct Alcohol Fuel Cells (DAFC), formed with a catalysed carbon substrate according to claims 25 - 26, containing nickel.

29. Anodes for Direct Oxidation Fuel Cells (DOFC) or Direct Alcohol Fuel Cells (DAFC) capable of producing open circuit voltages (OCV) as high as 1.13 V and powers as high as 160 mW/cm^2 at ambient temperature and pressure.

30. Cathodes for Direct Oxidation Fuel Cells (DOFC) or Direct Alcohol Fuel Cells (DAFC) capable of producing open circuit voltages (OCV) as high as 1.13 V and powers as high as 160 mW/cm^2 at ambient temperature and pressure.

31. Anodes for Polymer Electrolyte Fuel cells (PEFC) fuelled with H_2 containing iron, cobalt and nickel in a preferred stoichiometric ratio and overall metal loading between 0.5 and 8 wt %, capable of producing open circuit voltages (OCV) as high as 1.18 V and powers as high as 300 mW/cm^2.

32. Cathodes for Polymer Electrolyte Fuel cells (PEFC) fuelled with H_2 containing nickel in loadings between 0.5-7 wt %, and capable of producing open circuit voltages (OCV) as high as 1.18 V and powers as high as 300 mW/cm^2.

33. Fuel cell comprising electrodes according to Claims 10 - 12 and 27 – 32.